



US009469747B2

(12) **United States Patent**
Hampson et al.

(10) **Patent No.:** **US 9,469,747 B2**
(45) **Date of Patent:** ***Oct. 18, 2016**

(54) **MINERAL WOOL INSULATION**
(75) Inventors: **Carl Hampson**, St. Helens (GB); **Gert Mueller**, New Palestine, IN (US); **Charles Appley**, Cumberland, IN (US)
(73) Assignees: **Knauf Insulation SPRL**, Vise (BE); **Knauf Insulation, Inc.**, Shelbyville, IN (US)
(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 210 days.
This patent is subject to a terminal disclaimer.

C08L 101/06 (2006.01)
D04H 1/4218 (2012.01)
C09D 201/06 (2006.01)
C09D 199/00 (2006.01)
E04B 1/76 (2006.01)
C03C 25/32 (2006.01)
C03C 25/34 (2006.01)
C08L 101/02 (2006.01)
C09D 197/02 (2006.01)
C09D 201/02 (2006.01)
C08H 8/00 (2010.01)
C08L 97/02 (2006.01)
D04H 1/4209 (2012.01)
D04H 1/64 (2012.01)
C09K 3/00 (2006.01)

(21) Appl. No.: **12/671,922**
(22) PCT Filed: **Aug. 1, 2008**
(86) PCT No.: **PCT/EP2008/060178**
§ 371 (c)(1),
(2), (4) Date: **Apr. 15, 2011**
(87) PCT Pub. No.: **WO2009/019232**
PCT Pub. Date: **Feb. 12, 2009**

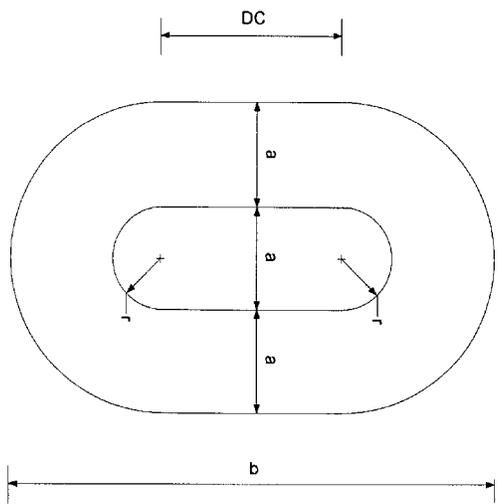
(52) **U.S. Cl.**
CPC *C08K 5/175* (2013.01); *C03C 25/32* (2013.01); *C03C 25/321* (2013.01); *C03C 25/34* (2013.01); *C08H 8/00* (2013.01); *C08L 97/02* (2013.01); *C08L 99/00* (2013.01); *C08L 101/025* (2013.01); *C08L 101/06* (2013.01); *C09D 197/02* (2013.01); *C09D 199/00* (2013.01); *C09D 201/025* (2013.01); *C09D 201/06* (2013.01); *C09K 3/00* (2013.01); *D04H 1/4209* (2013.01); *D04H 1/4218* (2013.01); *D04H 1/64* (2013.01); *E04B 1/7658* (2013.01); *E04B 1/7662* (2013.01)

(65) **Prior Publication Data**
US 2011/0260094 A1 Oct. 27, 2011

(58) **Field of Classification Search**
CPC .. *C08L 97/02*; *C08L 101/025*; *C08L 101/06*; *C08L 99/00*; *C08L 2666/02*; *C03C 25/32*; *C03C 25/321*; *C03C 25/34*; *C03C 17/28*; *C08H 8/00*; *C09D 197/02*; *C09D 199/00*; *C09D 201/025*; *C09D 201/06*; *C09K 3/00*; *D04H 1/42*; *D04H 1/64*; *D04H 1/4209*; *D04H 1/4218*; *D04H 1/587*; *D04H 1/641*; *C08K 5/175*; *C08K 7/14*; *C08K 3/40*; *E04B 1/7658*; *E04B 1/7662*; *E04B 1/78*; *E04B 1/84*; *Y10T 428/31971*; *Y10T 442/60*; *Y10T 442/691*
USPC 106/217.6, 217.9; 427/384
See application file for complete search history.

(30) **Foreign Application Priority Data**
Aug. 3, 2007 (GB) 0715100.4
Apr. 29, 2008 (GB) 0807777.8
Jun. 6, 2008 (GB) 0810297.2

(51) **Int. Cl.**
E04B 1/74 (2006.01)
D04H 3/00 (2012.01)
C08K 5/17 (2006.01)
C08L 99/00 (2006.01)



(56)

References Cited

U.S. PATENT DOCUMENTS

1,801,052	A	4/1931	Meigs	4,631,226	A	12/1986	Jellinek
1,801,053	A	4/1931	Meigs	4,654,259	A	3/1987	Stofko
1,886,353	A	11/1932	Novotny et al.	4,668,716	A	5/1987	Pepe et al.
1,902,948	A	3/1933	Castle	4,692,478	A	9/1987	Viswanathan et al.
1,964,263	A	6/1934	Krenke	4,714,727	A	12/1987	Hume, III
2,198,874	A	4/1940	Leighton	4,720,295	A	1/1988	Bronstein
2,215,825	A	9/1940	Wallace	4,754,056	A	6/1988	Ansel et al.
2,261,295	A	11/1941	Schlack	4,761,184	A	8/1988	Markessini
2,362,086	A	11/1944	Eastes	4,780,339	A	10/1988	Lacourse
2,371,990	A	3/1945	Hanford	4,828,643	A	5/1989	Newman
2,392,105	A	1/1946	Sussman	4,845,162	A	7/1989	Schmitt et al.
2,442,989	A	6/1948	Sussman	4,906,237	A	3/1990	Johansson et al.
2,500,665	A	3/1950	Courtright	4,912,147	A	3/1990	Pfoehler et al.
2,518,956	A	8/1950	Sussman	4,918,861	A	4/1990	Carpenter
2,875,073	A	2/1959	Gogek	4,923,980	A	5/1990	Blomberg
2,894,920	A	7/1959	Ramos	4,950,444	A	8/1990	Deboufie
2,965,504	A	12/1960	Gogek	4,988,780	A	1/1991	Das
3,038,462	A	6/1962	Bohdan	4,992,519	A	2/1991	Mukherjee
3,138,473	A	6/1964	Floyd	5,001,202	A	3/1991	Denis
3,231,349	A	1/1966	Stalego	5,013,405	A	5/1991	Izard
3,232,821	A	2/1966	Moore et al.	5,037,930	A	8/1991	Shih
3,297,419	A	1/1967	Eyre	5,041,595	A	8/1991	Yang et al.
3,513,001	A	5/1970	Woodhead	5,089,342	A	2/1992	Dhein
3,551,365	A	12/1970	Matalon	5,095,054	A	3/1992	Lay et al.
3,784,408	A	1/1974	Jaffe	5,106,615	A	4/1992	Dikstein
3,791,807	A	2/1974	Etzel et al. 65/451	5,114,004	A	5/1992	Isono et al.
3,802,897	A	4/1974	Voigt et al.	5,123,949	A	6/1992	Thiessen
3,809,664	A	5/1974	Fanta et al.	5,124,369	A	6/1992	Vandichel et al.
3,826,767	A	7/1974	Hoover et al.	5,128,407	A	7/1992	Layton
3,856,606	A	12/1974	Fan et al.	5,143,582	A	9/1992	Arkens
3,867,119	A	2/1975	Kasuga et al. 65/498	5,151,465	A	9/1992	Le-Khac
3,907,724	A	9/1975	Higginbottom	5,167,738	A	12/1992	Bichot
3,911,048	A	10/1975	Vargiu et al.	5,198,492	A	3/1993	Stack
3,919,134	A	11/1975	Higginbottom	5,217,741	A	6/1993	Kawachi
3,922,466	A	11/1975	Bell	5,218,048	A	6/1993	Abe
3,955,031	A	5/1976	Jones	5,240,498	A	8/1993	Matalon
3,956,204	A	5/1976	Higginbottom	5,278,222	A	1/1994	Stack
3,961,081	A	6/1976	McKenzie	5,300,144	A	4/1994	Adams
3,971,807	A	7/1976	Brack	5,300,192	A	4/1994	Hansen
4,014,726	A	3/1977	Fargo 156/167	5,308,896	A	5/1994	Hansen et al.
4,028,290	A	6/1977	Reid	5,318,990	A	6/1994	Strauss
4,048,127	A	9/1977	Gibbons et al.	5,336,753	A	8/1994	Jung et al.
4,054,713	A	10/1977	Sakaguchi et al.	5,336,755	A	8/1994	Pape
4,085,076	A	4/1978	Gibbons	5,336,766	A	8/1994	Koga
4,097,427	A	6/1978	Aitken et al.	5,340,868	A	8/1994	Strauss et al.
4,107,379	A	8/1978	Stofko	5,352,480	A	10/1994	Hansen
4,109,057	A	8/1978	Nakamura	5,371,194	A	12/1994	Ferretti
4,144,027	A	3/1979	Habib	5,387,665	A	2/1995	Misawa et al.
4,148,765	A	4/1979	Nelson	5,389,716	A	2/1995	Graves
4,183,997	A	1/1980	Stofko	5,393,849	A	2/1995	Srinivasan et al.
4,184,986	A	1/1980	Krasnobajew	5,416,139	A	5/1995	Zeiszler
4,186,053	A	1/1980	Krasnobajew	5,421,838	A	6/1995	Gosset
4,201,857	A	5/1980	Krasnobajew	5,424,418	A	6/1995	Duflot
4,217,414	A	8/1980	Walon	5,434,233	A	7/1995	Kiely et al.
4,233,432	A	11/1980	Curtis, Jr.	5,447,977	A	9/1995	Hansen
4,246,367	A	1/1981	Curtis, Jr.	5,470,843	A	11/1995	Stahl
4,259,190	A	3/1981	Fahey	5,480,973	A	1/1996	Goodlad et al.
4,265,963	A	5/1981	Matalon	5,492,756	A	2/1996	Seale
4,278,573	A	7/1981	Tessler	5,498,662	A	3/1996	Tanaka et al.
4,296,173	A	10/1981	Fahey	5,534,612	A	7/1996	Taylor
4,301,310	A	11/1981	Wagner	5,536,766	A	7/1996	Seyffer et al.
4,310,585	A	1/1982	Shannon	5,538,783	A	7/1996	Hansen
4,322,523	A	3/1982	Wagner	5,543,215	A	8/1996	Hansen
4,330,443	A	5/1982	Rankin	5,545,279	A	8/1996	Hall
4,333,484	A	6/1982	Keritsis	5,547,541	A	8/1996	Hansen et al.
4,357,194	A	11/1982	Stofko	5,547,745	A	8/1996	Hansen
4,361,588	A	11/1982	Herz	5,550,189	A	8/1996	Qin
4,379,101	A	4/1983	Smith	5,554,730	A	9/1996	Woiszwillo
4,393,019	A	7/1983	Geimer	5,562,740	A	10/1996	Cook
4,396,430	A	8/1983	Matalon	5,571,618	A	11/1996	Hansen et al.
4,400,496	A	8/1983	Butler et al.	5,578,678	A	11/1996	Hartmann et al.
4,464,523	A	8/1984	Neigel et al.	5,580,856	A	12/1996	Prestrelski
4,506,684	A	3/1985	Keritsis	5,582,682	A	12/1996	Ferretti
4,520,143	A	5/1985	Jellinek	5,583,193	A	12/1996	Aravindakshan et al.
4,524,164	A	6/1985	Viswanathan et al.	5,589,256	A	12/1996	Hansen
				5,589,536	A	12/1996	Golino

US 9,469,747 B2

5,607,759 A	3/1997	Hansen	6,340,411 B1	1/2002	Hansen
5,608,011 A	3/1997	Eck	6,348,530 B1	2/2002	Reck
5,609,727 A	3/1997	Hansen et al.	6,365,079 B1	4/2002	Winkler
5,614,570 A	3/1997	Hansen et al.	6,372,077 B1	4/2002	Teclé
5,620,940 A	4/1997	Birbara et al.	6,379,739 B1	4/2002	Formanek et al.
5,621,026 A	4/1997	Tanaka et al.	6,395,856 B1	5/2002	Petty et al.
5,633,298 A	5/1997	Arfaei et al.	6,403,665 B1	6/2002	Sieker
5,641,561 A	6/1997	Hansen	6,407,225 B1	6/2002	Mang
5,643,978 A	7/1997	Darwin et al.	6,410,036 B1	6/2002	De Rosa
5,645,756 A	7/1997	Dubin et al.	6,440,204 B1	8/2002	Rogols et al.
5,660,904 A	8/1997	Andersen	6,461,553 B1	10/2002	Hansen
5,661,213 A	8/1997	Arkens et al.	6,468,442 B2	10/2002	Bytnar
5,670,585 A	9/1997	Taylor	6,468,730 B2	10/2002	Fujiwara et al.
5,672,418 A	9/1997	Hansen	6,469,120 B1	10/2002	Elfersy
5,672,659 A	9/1997	Shalaby	6,475,552 B1	11/2002	Shah
5,690,715 A	11/1997	Schiwek	6,482,875 B2	11/2002	Lorenz et al.
5,691,060 A	11/1997	Levy	6,495,656 B1	12/2002	Haile et al.
5,693,411 A	12/1997	Hansen et al.	6,521,339 B1	2/2003	Hansen
5,719,092 A	2/1998	Arrington	6,525,009 B2	2/2003	Sachdev et al.
5,719,228 A	2/1998	Taylor	6,538,057 B1	3/2003	Wildburg
5,756,580 A	5/1998	Natori et al.	6,547,867 B2	4/2003	Rogols
5,763,524 A	6/1998	Arkens	6,555,616 B1	4/2003	Helbing
5,788,243 A	8/1998	Harshaw	6,559,302 B1	5/2003	Shah
5,788,423 A	8/1998	Perkins	6,562,267 B1	5/2003	Hansen
5,807,364 A	9/1998	Hansen	6,596,103 B1	7/2003	Hansen
5,855,987 A	1/1999	Margel et al.	6,613,378 B1	9/2003	Erhan et al.
5,863,985 A	1/1999	Shalaby	6,638,882 B1	10/2003	Helbing et al.
5,885,337 A	3/1999	Nohr et al.	6,638,884 B2	10/2003	Quick et al.
5,895,804 A	4/1999	Lee et al.	6,699,945 B1	3/2004	Chen
5,905,115 A	5/1999	Luitjes	6,706,853 B1	3/2004	Stanssens
5,916,503 A	6/1999	Rettenbacher	6,719,862 B2	4/2004	Quick
5,919,528 A	7/1999	Huijs	6,730,730 B1	5/2004	Hansen
5,919,831 A	7/1999	Philipp	6,753,361 B2	6/2004	Kroner et al.
5,922,403 A	7/1999	Teclé	6,818,694 B2*	11/2004	Hindi et al. 524/446
5,925,722 A	7/1999	Exner et al.	6,821,547 B2	11/2004	Shah
5,929,184 A	7/1999	Holmes-Farley et al.	6,852,247 B2	2/2005	Bytnar
5,929,196 A	7/1999	Kissel	6,858,074 B2	2/2005	Anderson et al.
5,932,344 A	8/1999	Ikemoto et al.	6,861,495 B2	3/2005	Barsotti et al.
5,932,665 A	8/1999	DePorter et al.	6,864,044 B2	3/2005	Ishikawa et al.
5,932,689 A	8/1999	Arkens et al.	6,878,800 B2	4/2005	Husemoen
5,942,123 A	8/1999	McArdle	6,884,849 B2	4/2005	Chen
5,954,869 A	9/1999	Elfersy	6,955,844 B2	10/2005	Tagge et al.
5,977,224 A	11/1999	Cheung et al.	6,962,714 B2	11/2005	Hei
5,977,232 A	11/1999	Arkens et al.	6,989,171 B2	1/2006	Portman
5,981,719 A	11/1999	Woiszwillo et al.	6,992,203 B2	1/2006	Trusovs
5,983,586 A	11/1999	Berdan, II et al.	7,018,490 B2	3/2006	Hansen
5,990,216 A	11/1999	Cai et al.	7,029,717 B1	4/2006	Ojima et al.
5,993,709 A	11/1999	Bonomo	7,067,579 B2	6/2006	Taylor et al.
6,022,615 A	2/2000	Rettenbacher	7,083,831 B1	8/2006	Koch
6,067,821 A	5/2000	Jackson	7,090,745 B2	8/2006	Beckman et al.
6,071,549 A	6/2000	Hansen	7,141,626 B2	11/2006	Rodrigues et al.
6,071,994 A	6/2000	Hummerich	7,144,474 B1	12/2006	Hansen
6,072,086 A	6/2000	James et al.	7,195,792 B2	3/2007	Boston et al.
6,077,883 A	6/2000	Taylor et al.	7,201,778 B2	4/2007	Smith et al.
6,090,925 A	7/2000	Woiszwillo et al.	7,201,825 B2	4/2007	Dezutter
6,114,033 A	9/2000	Ikemoto et al.	7,202,326 B2	4/2007	Kuroda
6,114,464 A	9/2000	Reck et al.	7,241,487 B2	7/2007	Taylor
6,133,347 A	10/2000	Vickers, Jr.	7,458,235 B2	12/2008	Beaufils
6,136,916 A	10/2000	Arkens et al.	7,514,027 B2	4/2009	Horres
6,139,619 A	10/2000	Zaretskiy	7,655,711 B2	2/2010	Swift
6,143,243 A	11/2000	Gershun	7,772,347 B2	8/2010	Swift
6,171,444 B1	1/2001	Nigam	7,795,354 B2	9/2010	Srinivasan
6,171,654 B1	1/2001	Salsman et al.	7,803,879 B2	9/2010	Srinivasan
6,180,037 B1	1/2001	Anderson	7,807,771 B2	10/2010	Swift
6,194,512 B1	2/2001	Chen	7,842,382 B2	11/2010	Helbing
6,210,472 B1	4/2001	Kwan et al.	7,854,980 B2	12/2010	Jackson
6,221,958 B1	4/2001	Shalaby	7,883,693 B2	2/2011	Sehl
6,221,973 B1	4/2001	Arkens et al.	7,888,445 B2	2/2011	Swift
6,231,721 B1	5/2001	Quick	7,947,765 B2	5/2011	Swift
6,274,661 B1	8/2001	Chen	8,114,210 B2	2/2012	Hampson
6,281,298 B1	8/2001	Papsin, Jr.	8,182,648 B2	5/2012	Swift
6,299,677 B1	10/2001	Johnson	8,211,923 B2	7/2012	Wagner
6,299,936 B1	10/2001	Reck	8,372,900 B2	2/2013	Shoostari
6,307,732 B1	10/2001	Tsubaki	8,377,564 B2	2/2013	Shoostari
6,310,227 B1	10/2001	Sarama et al.	8,501,838 B2	8/2013	Jackson
6,313,102 B1	11/2001	Colaco et al.	8,680,224 B2	3/2014	Zhang
6,319,683 B1	11/2001	James et al.	8,691,934 B2	4/2014	Helbing
6,331,350 B1	12/2001	Taylor et al.	8,900,495 B2	12/2014	Pacorel
6,331,513 B1	12/2001	Zaid	2001/0017427 A1	8/2001	Rosthauser

2001/0046824	A1	11/2001	Nigam	2007/0123679	A1	5/2007	Swift et al.
2002/0000100	A1	1/2002	Burg	2007/0123680	A1	5/2007	Swift
2002/0025435	A1	2/2002	Hansen	2007/0129522	A1	6/2007	Burckhardt
2002/0026025	A1	2/2002	Kuo	2007/0142596	A1	6/2007	Swift
2002/0028857	A1	3/2002	Holy	2007/0158022	A1	7/2007	Heep
2002/0032253	A1	3/2002	Lorenz et al.	2007/0184740	A1	8/2007	Keller
2002/0042473	A1	4/2002	Trollsas	2007/0191574	A1	8/2007	Miller
2002/0091185	A1	7/2002	Taylor et al.	2007/0270070	A1	11/2007	Hamed
2002/0096278	A1	7/2002	Foster	2007/0292618	A1	12/2007	Srinivasan
2002/0123598	A1	9/2002	Sieker	2007/0292619	A1	12/2007	Srinivasan
2002/0130439	A1	9/2002	Kroner	2007/0298274	A1	12/2007	Eriksson
2002/0161108	A1	10/2002	Schultz et al.	2008/0009209	A1	1/2008	Clamen
2002/0197352	A1	12/2002	Portman	2008/0051539	A1	2/2008	Kelly
2003/0005857	A1	1/2003	Minami et al.	2008/0060551	A1	3/2008	Crews
2003/0040239	A1	2/2003	Toas	2008/0081138	A1	4/2008	Moore
2003/0044513	A1	3/2003	Shah	2008/0108741	A1	5/2008	Van Herwijnen et al.
2003/0066523	A1	4/2003	Lewis	2008/0160260	A1	7/2008	Wada
2003/0071879	A1	4/2003	Swenson	2008/0160302	A1	7/2008	Asrar
2003/0116294	A1	6/2003	Kehrer	2008/0194738	A1	8/2008	Crews
2003/0134945	A1	7/2003	Capps	2009/0169867	A1	7/2009	Kelly
2003/0148084	A1	8/2003	Trocino	2009/0170978	A1	7/2009	Kelly
2003/0153690	A1	8/2003	Husemoen	2009/0227732	A1	9/2009	Glockner
2003/0185991	A1	10/2003	Wigger	2009/0301972	A1	12/2009	Hines
2003/0203117	A1	10/2003	Bartkowiak	2009/0304919	A1	12/2009	Wagner
2004/0002567	A1	1/2004	Chen	2009/0306255	A1	12/2009	Patel
2004/0019168	A1	1/2004	Soerens et al.	2009/0324915	A1	12/2009	Swift
2004/0024170	A1	2/2004	Husemoen	2010/0029160	A1	2/2010	Srinivasan
2004/0033269	A1	2/2004	Hei	2010/0058661	A1	3/2010	Jackson
2004/0033747	A1	2/2004	Miller et al.	2010/0080976	A1	4/2010	Jackson
2004/0034154	A1	2/2004	Tutin	2010/0084598	A1	4/2010	Jackson
2004/0038017	A1	2/2004	Tutin et al.	2010/0086726	A1	4/2010	Jackson
2004/0048531	A1	3/2004	Belmares	2010/0087571	A1	4/2010	Jackson
2004/0077055	A1	4/2004	Fosdick et al.	2010/0098947	A1	4/2010	Inoue
2004/0079499	A1	4/2004	Dezutter	2010/0129640	A1	5/2010	Kelly
2004/0087024	A1	5/2004	Bellocq	2010/0130649	A1	5/2010	Swift
2004/0122166	A1	6/2004	O—Brien-Bernini et al.	2010/0175826	A1	7/2010	Huenig
2004/0131874	A1	7/2004	Tutin	2010/0210595	A1	8/2010	Wagner
2004/0144706	A1	7/2004	Beaufils	2010/0222463	A1	9/2010	Brady
2004/0152824	A1	8/2004	Dobrowolski	2010/0222566	A1	9/2010	Fosdick
2004/0161993	A1	8/2004	Tripp	2010/0282996	A1	11/2010	Jaffrennou
2004/0209851	A1	10/2004	Nelson	2010/0301256	A1	12/2010	Hampson
2004/0213930	A1	10/2004	Halabisky	2010/0320113	A1	12/2010	Swift
2004/0220368	A1	11/2004	Li	2011/0021672	A1	1/2011	Crews
2004/0249066	A1	12/2004	Heinzman et al.	2011/0039111	A1	2/2011	Shoostari
2004/0254285	A1	12/2004	Rodrigues et al.	2011/0040010	A1	2/2011	Shoostari
2004/0260082	A1	12/2004	Van Der Wilden	2011/0042303	A1	2/2011	Shoostari
2005/0001198	A1	1/2005	Bytnar	2011/0045966	A1	2/2011	Shoostari
2005/0017394	A1	1/2005	Hochsmann	2011/0089074	A1	4/2011	Jackson
2005/0027283	A1	2/2005	Richard	2011/0135937	A1	6/2011	Swift
2005/0033037	A1	2/2005	Trusovs	2011/0190425	A1	8/2011	Swift
2005/0048212	A1	3/2005	Clamen	2011/0220835	A1	9/2011	Swift
2005/0059770	A1	3/2005	Srinivasan	2011/0256790	A1	10/2011	Toas
2005/0171085	A1	8/2005	Pinto et al.	2011/0260094	A1	10/2011	Hampson
2005/0196421	A1	9/2005	Hunter et al.	2011/0262648	A1	10/2011	Lee
2005/0202224	A1	9/2005	Helbing et al.	2011/0263757	A1	10/2011	Rand
2005/0208852	A1	9/2005	Weber	2011/0306726	A1	12/2011	Bailey
2005/0215153	A1	9/2005	Cossement et al.	2012/0133073	A1	5/2012	Pacorel
2005/0245669	A1	11/2005	Clungeon	2012/0156954	A1	6/2012	Eckert
2005/0275133	A1	12/2005	Cabell et al.	2013/0029150	A1	1/2013	Appley
2005/0288479	A1	12/2005	Kuroda	2013/0032749	A1	2/2013	Jaffrennou et al.
2006/0005580	A1	1/2006	Espiard	2013/0047888	A1	2/2013	Mueller
2006/0044302	A1	3/2006	Chen	2013/0059075	A1	3/2013	Appley
2006/0099870	A1	5/2006	Garcia et al.	2013/0082205	A1	4/2013	Mueller
2006/0111480	A1	5/2006	Hansen	2013/0174758	A1	7/2013	Mueller
2006/0124538	A1	6/2006	Morcrette	2013/0234362	A1	9/2013	Swift
2006/0135433	A1	6/2006	Murray et al.	2013/0236650	A1	9/2013	Swift
2006/0141177	A1	6/2006	Ligtenberg	2013/0237113	A1	9/2013	Swift
2006/0179892	A1	8/2006	Horres	2013/0244524	A1	9/2013	Swift
2006/0188465	A1	8/2006	Perrier	2014/0091247	A1	4/2014	Jackson
2006/0198954	A1	9/2006	Frechem	2014/0134909	A1	5/2014	Guo et al.
2006/0231487	A1	10/2006	Bartley	2014/0357787	A1	12/2014	Jobber et al.
2006/0252855	A1	11/2006	Pisanova et al.				
2006/0281622	A1	12/2006	Maricourt				
2007/0006390	A1	1/2007	Clamen et al.				
2007/0009582	A1	1/2007	Madsen et al.				
2007/0027281	A1	2/2007	Michl	AU	8538765	8/1985	
2007/0027283	A1	2/2007	Swift et al.	AU	9640921	7/1997	
2007/0039520	A1	2/2007	Crews	CA	1090026	11/1980	
2007/0082983	A1	4/2007	Crews	CA	2037214	9/1991	
				CA	2232334	11/1998	

FOREIGN PATENT DOCUMENTS

CA	2458333	12/1999	WO	99/47765	9/1999
CA	2278946	1/2000	WO	9960042	11/1999
CA	2470783	12/2004	WO	9960043	11/1999
CN	1251738	5/2000	WO	00/62628	10/2000
DE	1905054	8/1969	WO	0058085	10/2000
DE	4142261	6/1993	WO	0114491	3/2001
DE	4233622	4/1994	WO	0159026	8/2001
DE	4308089	9/1994	WO	0200429	1/2002
DE	102004033561	9/2005	WO	03029496	4/2003
DE	102005023431	11/2006	WO	03/071879	9/2003
EP	0044614	1/1982	WO	03106561	12/2003
EP	0099801	2/1984	WO	2004/076734	9/2004
EP	354023	2/1990	WO	2005087837	9/2005
EP	0461995	12/1991	WO	2006/044302	4/2006
EP	0 524 518	7/1992	WO	2006/136614	12/2006
EP	0 547 819	12/1992	WO	WO2007/014236	2/2007
EP	0 583 086	7/1993	WO	WO2007/024020	3/2007
EP	0 672 720	3/1995	WO	2007050964	5/2007
EP	0 714 754	6/1996	WO	2007112335	10/2007
EP	0 826 710	8/1997	WO	2008089847	7/2008
EP	796681	9/1997	WO	2008089851	7/2008
EP	0 873 976	4/1998	WO	2008141201	11/2008
EP	856494	8/1998	WO	2009019235	2/2009
EP	878135	11/1998	WO	2010139899	12/2010
EP	0 882 756	12/1998	WO	2011019590	2/2011
EP	0 911 361	4/1999	WO	2011019593	2/2011
EP	915811	5/1999	WO	2011019597	2/2011
EP	936060	8/1999	WO	2011019598	2/2011
EP	976866	2/2000	WO	2011022224	2/2011
EP	0 990 729	4/2000	WO	2011022226	2/2011
EP	1 038 433	9/2000	WO	2011022227	2/2011
EP	1 193 288	9/2001	WO	2011138458	11/2011
EP	1 225 193	7/2002	WO	2011138459	11/2011
EP	1084167	9/2002	WO	2013150123	10/2013
EP	1268702	1/2003			
EP	1382642	1/2004			
EP	1 486 547	6/2004			
EP	1522642	4/2005			
EP	1698598	9/2006			
EP	1767566	4/2007			
EP	2223941	9/2010			
EP	2253663	11/2010			
FR	2 614 388	10/1988			
GB	809675	3/1959			
GB	926749	5/1963			
GB	1391172	4/1975			
GB	1469331	4/1977			
GB	1512066	5/1978			
GB	1525541	9/1978			
GB	2047258	11/1980			
GB	2 078 805	1/1982			
GB	2173523	10/1986			
GB	2251438	7/1992			
JP	53113784	10/1978			
JP	57-101100	6/1982			
JP	58-11193	1/1983			
JP	61195647	8/1986			
JP	3-173680	7/1991			
JP	05186635	7/1993			
JP	7-34023	2/1995			
JP	09157627	6/1997			
JP	10234314	9/1998			
JP	11035491	2/1999			
JP	11181690	7/1999			
JP	2000327841	11/2000			
JP	2002-293576	9/2002			
JP	2003147276	5/2003			
JP	2003238921	8/2003			
JP	2004-60058	2/2004			
JP	2005-306919	11/2005			
NZ	549563	1/2008			
RU	1765996	8/1995			
SU	374400	3/1973			
WO	9007541	7/1990			
WO	9212198	7/1992			
WO	WO94/17004	* 8/1994 C03C 25/10		
WO	9534517	12/1995			
WO	9749646	12/1997			
WO	9936368	7/1999			

OTHER PUBLICATIONS

Ames, J. M., "The Maillard Browning Reaction—an Update", *Chemistry & Industry*, No. 17, 1988, 4 pages.

"Gamma-aminopropyltrimethoxysilane", *Hawley's Condensed Chemical Dictionary*, 14th Edition, John Wiley & Sons, Inc., 2002, 1 page.

English Translation of Japanese Abstract for 58011193, Jan. 21, 1983, 1 page.

English Translation of Japanese Abstract for 03173680, Jul. 26, 1991, 1 page.

English Translation of Japanese Abstract for 07034023, Feb. 3, 1995, 1 page.

English Translation of Russian Abstract for 374400, Mar. 20, 1973, 1 page.

English Translation of Japanese Abstract for 2004-60058, Feb. 26, 2004, 1 page.

English Translation of French Abstract for 2614388, Oct. 28, 1988, 1 page.

English Translation of Japanese Abstract for 2002-293576, Oct. 9, 2002, 2 pages.

English Translation of Japanese Abstract for 57-101100, Jun. 23, 1982, 1 page.

English Translation of European Abstract for 1038433, Sep. 27, 2000, 1 page.

International Search Report and Written Opinion for PCT/US2008/059730, completed Sep. 16, 2008.

Hodge, J.E., *Chemistry of Browning Reactions in Model Systems*, 1953, *J. Agric. Food Chem.*, vol. 1, No. 15, pp. 928-943.

International Search Report and Written Opinion for PCT/US2008/069046, completed Sep. 22, 2008.

International Search Report and Written Opinion for PCT/EP2008/060178, completed Oct. 14, 2008.

Office action for co-pending U.S. Appl. No. 12/524,512 (10 pages)—Mar. 23, 2016.

Office action for co-pending U.S. Appl. No. 12/524,539 (7 pages)—Mar. 23, 2016.

- Examiner's Answer in Ex Parte Reexamination of U.S. Pat. No. 7,888,445 (8 pages)—Mar. 23, 2016.
- Examiner's Answer in Ex Parte Reexamination of U.S. Pat. No. 7,772,347 (8 pages)—Mar. 23, 2016.
- Examiner's Answer in Ex Parte Reexamination of U.S. Pat. No. 7,854,980 (8 pages)—Mar. 22, 2016.
- Decision of PTAB in Inter Partes Reexamination of U.S. Pat. No. 7,888,445 (34 pages)—May 1, 2015.
- Decision of PTAB in Inter Partes Reexamination of U.S. Pat. No. 7,772,347 (36 pages)—May 1, 2015.
- Advisory Action in Ex Parte Reexamination of U.S. Pat. No. 7,888,445 (4 pages)—Oct. 6, 2015.
- Advisory Action in Ex Parte Reexamination of U.S. Pat. No. 7,772,347 (4 pages)—Oct. 6, 2015.
- Decision of PTAB regarding Institution of Inter Partes Review for U.S. Pat. No. 8,114,210 (20 pages)—Oct. 21, 2015.
- 2nd Petition For Inter Partes Review of U.S. Pat. No. D631,670 (62 pages, filed Nov. 2, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc.).
- Remand Order of PTAB in Inter Partes Reexamination of U.S. Pat. No. 7,888,445 (5 pages)—Dec. 9, 2015.
- Remand Order of PTAB in Inter Partes Reexamination of U.S. Pat. No. 7,772,347 (5 pages)—Dec. 9, 2015.
- Decision1 of PTAB declining Institution of Inter Partes Review for U.S. Pat. No. 8,940,089 (16 pages)—Dec. 17, 2015.
- Decision2 of PTAB declining Institution of Inter Partes Review for U.S. Pat. No. 8,940,089 (19 pages)—Dec. 17, 2015.
- Decision3 of PTAB declining Institution of Inter Partes Review for U.S. Pat. No. 8,940,089 (14 pages)—Dec. 17, 2015.
- Decision2 of PTAB regarding Institution of Inter Partes Review for U.S. Pat. No. D631,670 (27 pages)—May 9, 2016.
- Office action for co-pending U.S. Appl. No. 14/649,277 (9 pages)—Jul. 22, 2016.
- Decision re Opposition to AU 2006272595, issued from Australian Patent Office, Aug. 14, 2015, 25 pages.
- Decision re Opposition to EP 1732968, issued from the European Patent Office, Nov. 14, 2014, 5 pages.
- Opposition to EA 019802, submitted to Eurasian Patent Office on Dec. 26, 2014, 36 pages.
- Decision re Opposition to EA 019802, issued by Eurasian Patent Office on Aug. 18, 2015, 15 pages.
- Office action for co-pending U.S. Appl. No. 13/637,794 (8 pages)—Aug. 12, 2013.
- Office action for co-pending U.S. Appl. No. 13/637,794 (9 pages)—Mar. 26, 2014.
- Office action for co-pending U.S. Appl. No. 14/810,765 (7 pages)—Jan. 29, 2016.
- Decision1 of PTAB declining Institution of Inter Partes Review for U.S. Pat. No. 9,039,827 (16 pages)—Jan. 4, 2016.
- Decision2 of PTAB declining Institution of Inter Partes Review for U.S. Pat. No. 9,039,827 (19 pages)—Jan. 4, 2016.
- Decision3 of PTAB declining Institution of Inter Partes Review for U.S. Pat. No. 9,039,827 (14 pages)—Jan. 4, 2016.
- Decision of PTAB regarding Institution of Inter Partes Review for U.S. Pat. No. D631,670 (33 pages)—Jan. 12, 2016.
- File Wrapper re U.S. Pat. No. 2,965,504—Part 1 (10 pages).
- File Wrapper re U.S. Pat. No. 2,965,504—Part 2 (14 pages).
- File Wrapper re U.S. Pat. No. 2,965,504—Part 3 (14 pages).
- Gogek Attorney Comments re U.S. Pat. No. 2,965,504—Apr. 6, 1960 (3 pages).
- Gogek Affidavit Under Rule 132 re U.S. Pat. No. 2,965,504—Feb. 26, 1960 (3 pages).
- Advisory Action in Ex Parte Reexamination of U.S. Pat. No. 7,854,980 (4 pages)—Nov. 18, 2015.
- Office action for co-pending U.S. Appl. No. 12/524,502 (9 pages)—Sep. 21, 2012.
- Office action for co-pending U.S. Appl. No. 12/524,502 (9 pages)—Apr. 4, 2013.
- Office action for co-pending U.S. Appl. No. 13/696,452 (7 pages)—Jan. 13, 2015.
- Office action for co-pending U.S. Appl. No. 13/696,452 (9 pages)—Oct. 27, 2015.
- International Search Report for PCT/EP2008/060185, completed Oct. 23, 2008.
- International Search Report for PCT/EP2011/057363, completed Sep. 5, 2011.
- Agyei-Aye et al., "The Role of Anion in the the Reaction of Reducing Sugars with Ammonium Salts," *Carbohydrates Research* 2002, 337:2273-2277.
- Bjorksten et al., "Polyester Resin—Glass Fiber Laminates," *Industrial and Engineering Chemistry* (1954).
- Dow Corning, "A Guide to Silane Solutions," 2005.
- Knauf Data Sheet, 2006.
- Molasses Corporation, United States Sugar Corporation, <http://www.suga-lik.com/molasses/composition.html> (Sep. 29, 2003).
- Clamen, Guy, "Acrylic Thermosets: A Safe Alternative to Formaldehyde Resins," *Nonwovens World*, Apr.-May 2004, pp. 96-102.
- Opposition to AU 2006272595, Amended Statement of Grounds and Particulars, issued from Australian Patent Office, Jul. 6, 22 pages.
- Opposition to EP 1732968, Notice of Opposition: Prior Art, Scope of the Patent, Reasons for the Opposition, issued from European Patent Office, Mar. 8, 2012, 18 pages.
- Owens Corning Retiree Update: What Goes Around, Comes Around: A tale of Natural Binders, revised Mar. 20, 2013 p. 4.
- A.P. Bryant, "The Terminology of Sugars," *Industrial and Engineering Chemistry*, vol. 26, No. 2, p. 231, Feb. 1934.
- Food Flavor Chemistry (IIC140593), p. 162, Mar. 21, 2009 (English Abstract).
- Office action for co-pending U.S. Appl. No. 12/524,512 (7 pages)—Aug. 6, 2012.
- Office action for co-pending U.S. Appl. No. 12/524,512 (9 pages)—Apr. 1, 2013.
- Office action for co-pending U.S. Appl. No. 12/524,512 (14 pages)—Nov. 12, 2014.
- Office action for co-pending U.S. Appl. No. 12/524,512 (9 pages)—Jul. 10, 2015.
- Office action for co-pending U.S. Appl. No. 12/524,469 (7 pages)—Jun. 7, 2012.
- Office action for co-pending U.S. Appl. No. 12/524,469 (8 pages)—Jan. 29, 2013.
- Office action for co-pending U.S. Appl. No. 12/524,469 (7 pages)—Aug. 20, 2013.
- Office action for co-pending U.S. Appl. No. 12/524,469 (9 pages)—Jun. 9, 2014.
- Office action for co-pending U.S. Appl. No. 12/524,469 (9 pages)—Oct. 17, 2014.
- Office action for co-pending U.S. Appl. No. 12/524,469 (9 pages)—Jul. 23, 2015.
- Office action for co-pending U.S. Appl. No. 12/524,539 (13 pages)—Jun. 21, 2012.
- Office action for co-pending U.S. Appl. No. 12/524,539 (13 pages)—Jun. 6, 2013.
- Office action for co-pending U.S. Appl. No. 12/524,539 (12 pages)—Dec. 17, 2014.
- Office action for co-pending U.S. Appl. No. 12/524,539 (7 pages)—Jul. 15, 2015.
- Office action for co-pending U.S. Appl. No. 12/524,522 (4 pages)—Oct. 11, 2011.
- Office action for co-pending U.S. Appl. No. 12/667,718 (5 pages)—Sep. 3, 2013.
- Office action for co-pending U.S. Appl. No. 12/667,718 (6 pages)—Sep. 9, 2014.
- Office action for co-pending U.S. Appl. No. 13/388,408 (5 pages)—Aug. 15, 2013.
- Office action for co-pending U.S. Appl. No. 13/371,829 (9 pages)—Dec. 20, 2012.
- Office action for co-pending U.S. Appl. No. 13/371,829 (6 pages)—Jul. 12, 2013.
- Office action for co-pending U.S. Appl. No. 13/371,829 (6 pages)—Aug. 12, 2014.
- Office action for co-pending U.S. Appl. No. 13/696,439 (11 pages)—Jan. 8, 2014.
- Office action for co-pending U.S. Appl. No. 13/702,144 (6 pages)—Jan. 10, 2014.

Office action for co-pending U.S. Appl. No. 13/702,144 (7 pages)—Jul. 29, 2014.

Office action for co-pending U.S. Appl. No. 13/823,818 (9 pages)—Mar. 26, 2015.

Office action for co-pending U.S. Appl. No. 13/866,368 (16 pages)—Aug. 29, 2013.

Office action for co-pending U.S. Appl. No. 13/866,368 (11 pages)—Apr. 16, 2014.

Office action for co-pending U.S. Appl. No. 13/866,368 (8 pages)—Aug. 21, 2014.

Office action for co-pending U.S. Appl. No. 13/866,419 (14 pages)—Sep. 20, 2013.

Office action for co-pending U.S. Appl. No. 13/866,419 (10 pages)—Apr. 25, 2014.

Office action for co-pending U.S. Appl. No. 13/866,419 (8 pages)—Oct. 9, 2014.

Office action for co-pending U.S. Appl. No. 13/866,419 (8 pages)—Sep. 25, 2015.

Office action for co-pending U.S. Appl. No. 13/868,233 (23 pages)—Aug. 13, 2013.

Office action for co-pending U.S. Appl. No. 13/868,233 (12 pages)—Apr. 15, 2014.

Office action for co-pending U.S. Appl. No. 13/868,233 (8 pages)—Oct. 7, 2014.

Office action for co-pending U.S. Appl. No. 13/868,233 (8 pages)—Jul. 16, 2015.

Office action for co-pending U.S. Appl. No. 13/868,238 (8 pages)—Jul. 16, 2014.

Office action for co-pending U.S. Appl. No. 12/976,379 (7 pages)—Jan. 10, 2012.

Office action for co-pending U.S. Appl. No. 12/976,379 (6 pages)—Jul. 27, 2012.

Office action for co-pending U.S. Appl. No. 12/976,379 (9 pages)—Mar. 7, 2013.

Office action for co-pending U.S. Appl. No. 12/976,379 (8 pages)—Aug. 20, 2013.

Office action for co-pending U.S. Appl. No. 12/599,858 (8 pages)—May 11, 2011.

Office action for co-pending U.S. Appl. No. 13/341,542 (8 pages)—Dec. 26, 2012.

Office action for co-pending U.S. Appl. No. 13/341,542 (7 pages)—Feb. 10, 2014.

Office action for co-pending U.S. Appl. No. 14/026,394 (6 pages)—Aug. 14, 2014.

Office action for co-pending U.S. Appl. No. 14/272,556 (14 pages)—Nov. 20, 2014.

Office action for co-pending U.S. Appl. No. 14/272,556 (12 pages)—Sep. 17, 2015.

Other Information—Narrative of verbal disclosure of Brian Swift (1 page)—May 13, 2014.

Petition for Inter Partes Review of U.S. Pat. No. 8,114,210 (52 pages, filed Jun. 12, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc.).

Declaration of Dr. Frederick J. Hirsekorn Regarding U.S. Pat. No. 8,114,210 (58 pages, filed Jun. 12, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc. in connection with Petition for Inter Partes Review of U.S. Pat. No. 8,114,210).

Petition for Inter Partes Review of U.S. Pat. No. D631,670 (68 pages, filed Jun. 19, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc.).

1st Petition for Inter Partes Review of U.S. Pat. No. 8,940,089 (61 pages, filed Jul. 1, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc.).

Declaration of Dr. Frederick J. Hirsekorn Regarding U.S. Pat. No. 8,940,089 (70 pages, filed Jul. 1, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc. in connection with 1st Petition for Inter Partes Review of U.S. Pat. No. 8,940,089).

2nd Petition for Inter Partes Review of U.S. Pat. No. 8,940,089 (56 pages, filed Jul. 10, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc.).

Declaration of Dr. Frederick J. Hirsekorn Regarding U.S. Pat. No. 8,940,089 (67 pages, filed Jul. 10, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc. in connection with 2nd Petition for Inter Partes Review of U.S. Pat. No. 8,940,089).

3rd Petition for Inter Partes Review of U.S. Pat. No. 8,940,089 (62 pages, filed Jul. 17, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc.).

Declaration of Dr. Frederick J. Hirsekorn Regarding U.S. Pat. No. 8,940,089 (76 pages, filed Jul. 17, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc. in connection with 3rd Petition for Inter Partes Review of U.S. Pat. No. 8,940,089).

Declaration of Dr. Elam Leed (11 pages, filed Jul. 1, Jul. 10, and Jul. 17, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc. in connection with 1st, 2nd and 3rd Petition for Inter Partes Review of U.S. Pat. No. 8,940,089, respectively).

Declaration of Dr. Jonathan Vickers (10 pages, filed Jul. 1, Jul. 10, and Jul. 17, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc. in connection with 1st, 2nd and 3rd Petition for Inter Partes Review of U.S. Pat. No. 8,940,089, respectively).

1st Petition for Inter Partes Review of U.S. Pat. No. 9,039,827 (60 pages, filed Jul. 29, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc.).

Declaration of Dr. Frederick J. Hirsekorn Regarding U.S. Pat. No. 9,039,827 (72 pages, filed Jul. 29, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc. in connection with 1st Petition for Inter Partes Review of U.S. Pat. No. 9,039,827).

2nd Petition for Inter Partes Review of 2015 U.S. Pat. No. 9,039,827 (51 pages, filed Aug. 5, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc.).

Declaration of Dr. Frederick J. Hirsekorn Regarding U.S. Pat. No. 9,039,827 (65 pages, filed Aug. 5, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc. in connection with 2nd Petition for Inter Partes Review of U.S. Pat. No. 9,039,827).

3rd Petition for Inter Partes Review of 2015 U.S. Pat. No. 9,039,827 (57 pages, filed Aug. 7, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc.).

Declaration of Dr. Frederick J. Hirsekorn Regarding U.S. Pat. No. 9,039,827 (75 pages, filed Aug. 7, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc. in connection with 3rd Petition for Inter Partes Review of U.S. Pat. No. 9,039,827).

Declaration of Dr. Elam Leed (11 pages, filed Jul. 29, Aug. 5, and Aug. 7, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc. in connection with 1st, 2nd and 3rd Petition for Inter Partes Review of U.S. Pat. No. 9,039,827, respectively).

Declaration of Dr. Jonathan Vickers (10 pages, filed Jul. 29, Aug. 5, and Aug. 7, 2015 by Petitioners Johns Manville Corporation and Johns Manville, Inc. in connection with 1st, 2nd and 3rd Petition for Inter Partes Review of U.S. Pat. No. 9,039,827, respectively).

Final Rejection in Ex Parte Reexamination of U.S. Pat. No. 7,888,445 (20 pages)—Jul. 24, 2015.

Final Rejection in Ex Parte Reexamination of U.S. Pat. No. 7,772,347 (23 pages)—Jul. 24, 2015.

Final Rejection in Ex Parte Reexamination of U.S. Pat. No. 7,854,980 (31 pages)—Aug. 18, 2015.

Decision of PTAB in Inter Partes Reexamination of U.S. Pat. No. 7,854,980 (25 pages)—Jul. 30, 2015.

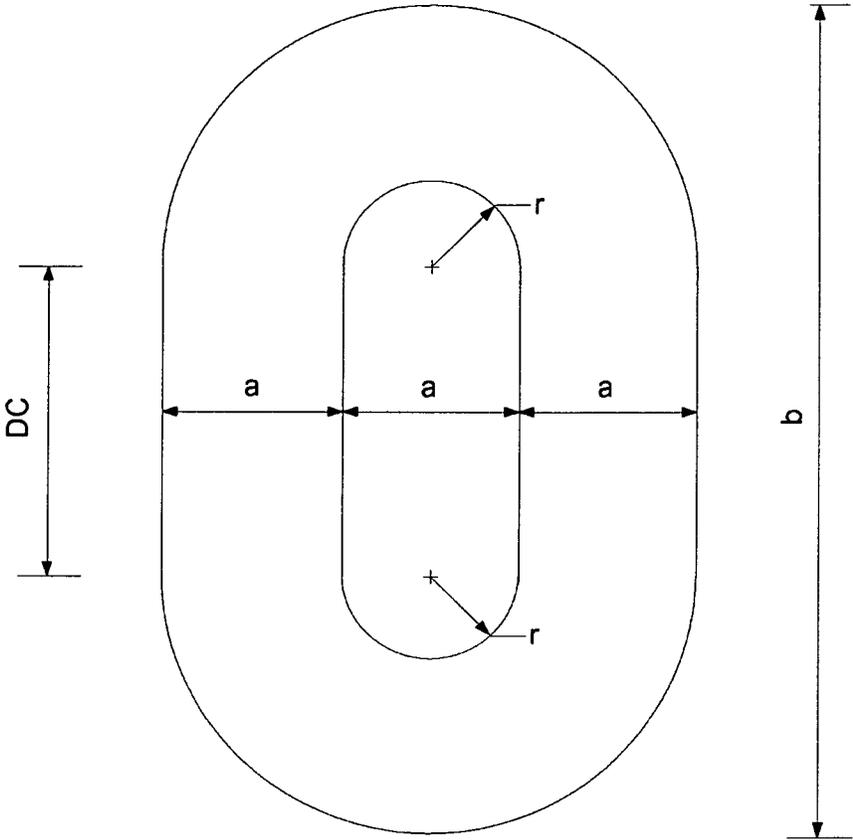
* cited by examiner

Primary Examiner — Shuangyi Abu Ali
(74) *Attorney, Agent, or Firm* — Knauf Insulation, Inc.;
James K. Blodgett

(57) **ABSTRACT**

A method of manufacturing a mineral fiber thermal insulation product comprises the sequential steps of: Forming mineral fibers from a molten mineral mixture; spraying a substantially formaldehyde free binder solution on to the mineral fibers, the binder solution comprising: a reducing sugar, an acid precursor derivable from an inorganic salt and a source of nitrogen; Collecting the mineral fibers to which the binder solution has been applied to form a batt of mineral fibers; and Curing the batt comprising the mineral fibers and the binder which is in contact with the mineral fibers by passing the batt through a curing oven so as to provide a batt of mineral fibers held together by a substantially water insoluble cured binder.

51 Claims, 1 Drawing Sheet



MINERAL WOOL INSULATION

This application is a U.S. national counterpart application of International Application Serial No. PCT/EP2008/060178, filed Aug. 1, 2008 under 35 USC §371, which claims priority to GB Patent Application Serial Number 0715100.4, filed Aug. 3, 2007, European GB Patent Application Serial Number 0807777.8, filed Apr. 29, 2008, and GB Patent Application Serial Number 0810297.2, filed Jun. 6, 2008, the entire disclosures of each of which are hereby incorporated herein by reference.

TECHNICAL FIELD

This invention relates to the manufacture of mineral wool insulation, for example glass wool or stone wool insulation, and to mineral wool insulation products.

BACKGROUND

WO 2007/014236 (incorporated herein by reference) discloses manufacture of mineral wool insulation products using binders which comprise Maillard reactants. One particular binder disclosed is based on a triammonium citrate-dextrose system derived from mixing dextrose monohydrate, anhydrous citric acid, water and aqueous ammonia. One of the many advantages of this binder system is that it is formaldehyde free.

SUMMARY

One aspect of the present invention provides a method of manufacturing a mineral fibre thermal insulation product in accordance with claim 1; further aspects of the inventions are defined in other independent claims. The dependent claims define alternative and/or preferred embodiments.

Binder solutions used in accordance with the present invention may be “substantially formaldehyde free”, that is to say that they liberate less than 5 ppm formaldehyde as a result of drying and/or curing (or appropriate tests simulating drying and/or curing). Such binder solutions are preferably “formaldehyde free”, that is the say they liberate less than 1 ppm formaldehyde in such conditions.

Insulation materials in accordance with the invention which incorporate binders may be “substantially formaldehyde free”, that is to say that they comprise less than 5 ppm or less than detectable limits of free formaldehyde and/or consist of materials which together comprise less than these amounts of free formaldehyde and/or release levels of formaldehyde in standardised tests adapted to simulate their ordinary use which allows them to be classified as having no or undetectable levels of formaldehyde release. Preferably, such products release less than 10 µg/m³, more preferably less than 5 µg/m³ of formaldehyde during the period of 24-48 hours from the start of testing in accordance with ISO 16000.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a plan view of a mineral fibre test sample, where r is radius=12.7 mm, DC is distance between centers=44.5 mm, a=25.4 mm, and b=121 mm.

DETAILED DESCRIPTION

It has been found that insulation materials made according to the present invention may have at least equivalent and indeed improved properties compared to, for example, products made using the tri-ammonium citrate-dextrose system of WO 2007/014236. WO 2007/014236 teaches binder

systems based, inter alia, on a combination of a carbohydrate (for example a reducing sugar), ammonia and a carboxylic acid and suggests that a Maillard type reaction may form the basis of the curing chemistry. It would have been thought that the nature of the acid used would have a significant effect upon the properties of the cured binder, particularly if the acid precursor and/or a derivative therefrom is incorporated into the structure of the cured binder. It is thus surprising that an acid precursor derivable from an inorganic salt should provide a suitable acid precursor in an otherwise apparently similar binder system.

Use of an acid precursor derivable from an inorganic salt may have significant advantages in terms of cost, availability and ease of handling. A particular advantage can be achieved by use of one or more inorganic ammonium salts, for example, an ammonium sulphate, an ammonium phosphate or an ammonium carbonate. An ammonium salt may provide the or part of the acid precursor and/or the or part of the source of nitrogen and/or the or part of a pH control system. An ammonium nitrate may also work; however, ammonium nitrate may oxidise aldehyde groups of the carbohydrate (for example in the case of dextrose) and/or require precautions to avoid explosions.

An ammonium sulphate is particularly advantageous but ammonium phosphate may be used in addition to or instead of this. Ammonium phosphate may be mono ammonium phosphate, di ammonium phosphate or tri ammonium phosphate; it may be an ammonium hydrogen phosphate. An ammonium carbonate, alone or in combination with the other materials disclosed herein, may also provide good results. The ammonium carbonate may be an ammonium bicarbonate.

The acid precursor, particularly when this consists essentially of inorganic ammonium salt(s), may make up at least 5%, preferably at least 7%, more preferably at least 9% by dry weight of the uncured binder solution; and/or less than 20%, preferably less than 18%, more preferably less than 16% by dry weight of the uncured binder solution.

The acid may comprise: a sulphuric acid, a phosphoric acid, a nitric acid or a weak acid.

The binder may comprise between 5%-25%, preferably 10% to 20%, more preferably 15% to 20% by dry weight of acid precursor (particularly where this is an inorganic ammonium salt) to carbohydrate (particularly when this is a sugar).

Where the binder comprises both an acid precursor derivable from an inorganic salt and an organic acid with the carbohydrate (particularly where this is a sugar), these may be present in the following amounts by dry weight with respect to the carbohydrate:

	Preferred	More preferred	Most preferred
acid precursor derivable from an inorganic salt	At least 2.5%	At least 5%	
organic acid	At least 2.5%	At least 5%	
Combination of organic acid and acid precursor derivable from an inorganic salt	5-25%	10-20%	15-20%

Where an organic acid is used, this is preferably derived from an ammonium salt. For example, an ammonium citrate, particularly tri-ammonium citrate may be used as a source of citric acid.

3

Prior art phenol formaldehyde binder systems for mineral wool insulation have been used with the addition of about 2% by weight ammonium sulphate as a curing agent. However, the chemistry of such phenol formaldehyde binder systems is not comparable to the binder systems of the present invention which are not based on phenol and/or formaldehyde and/or on other phenolics.

A carbohydrate may be used in the binder solution rather than specifically a reducing sugar and may comprise a monosaccharide, for example in its aldose or ketose form. Preferably, the carbohydrate comprises a sugar, more preferably a reducing sugar or a reactant that yields a reducing sugar in situ under thermal curing condition; it may comprise glucose (ie dextrose). The carbohydrate may comprise a carbohydrate having a reducing aldehyde. It is believed that the use of a reducing sugar and particularly dextrose gives particularly good results for the manufacture of mineral wool insulation products. The dextrose need not be 100% pure but use of a material having a dextrose equivalent value of at least 0.85, preferably at least 0.9 and more preferably at least 0.95 is thought to be advantageous. The dextrose equivalent value DE can be thought of as i) a measure of de-polymerization and is roughly: $DE=100/dp$ where dp stands for degree of polymerization or ii) the total amount of reducing sugars calculated as D-glucose (dextrose) on a dry basis.

Preferably, the binder solution and/or the binder is free or substantially free of starch; the presence of substantial quantities of starch is thought to increase the curing time and/or reduce the strength of the cured binder. The binder solution and/or the binder may be free or substantially free of proteins.

Industrial, non-food grade dextrose may be used as the reducing sugar; products such as Sirodex331 which is a 75% solids sugar solution obtainable from Tate and Lyle with a DE value of 94.5 may be used.

Particularly in the case where the reducing sugar consists essentially of dextrose and the acid precursor consists essentially of an ammonium salt, for example an ammonium sulphate, the ratio by dry weight of the amount of reducing sugar/the amount of acid precursor may be greater than or equal to 2.5 and/or less than or equal to 13.

The source of nitrogen may be an amine or an amine reactant; it may be derivable from the same source as the acid precursor, for example, from an inorganic ammonium salt. It is preferably ammonia in solution.

Precursors for and/or reactants which give the materials referred to may be used.

In one embodiment, the binder is derived essentially from a reducing sugar and an inorganic ammonium salt in aqueous solution.

In another embodiment, the binder may also comprise an organic acid, particularly a carboxylic acid; this may be a polycarboxylic acid, particularly a bi-carboxylic acid or tri-carboxylic acid, preferably citric acid; it is preferably monomeric. The combination of an organic acid (or a precursor a salt or an anhydride thereof) with an acid precursor derivable from an inorganic salt may present various advantages. Firstly, such a combination may reduce the risk of punking (which has been observed with such binders based solely on organic acids) whilst providing acceptable strength. Punking is a term of art in the mineral fibre insulation area which generally denotes a comparatively rapid oxidation of a binder with a concomitant generation of heat in a finished and generally packaged insulation product. Punking generally causes generation of fumes and discolouring of the insulation material. It may be

4

associated with exothermic reactions which increase the temperatures through the thickness of the insulation material; this may destroy the integrity of the insulation product and/or present a fire hazard.

Alternatively or additionally, the combination of an organic acid (or a precursor, a salt or an anhydride thereof) with an acid precursor derivable from an inorganic salt may moderate acid conditions occurring during curing and thus reduce the risk or tendency of such conditions to cause significant damage to the material being bound. Such a combination may be particularly advantageous as a binder for stone wool insulation whose fibres may be more susceptible to potential damage by acid than, for example, glass wool insulation.

In a further embodiment, the binder is derived essentially from: a carbohydrate; an inorganic ammonium salt; and an organic acid and/or organic acid precursor; in aqueous solution.

The term "consist or consisting essentially of" is intended to limit the scope of a claim to the specified materials or steps and those that do not materially affect the basic and novel characteristic(s) of the claimed invention.

Binders which comprise or consist essentially of the components described herein may include additives, for example, additives selected from: silanes, mineral oils, coupling agents, silicones or siloxanes (particularly for water repellency), silicon containing compounds, surfactants, hydrophilic additives, hydrophobic additives, waxes, substances useful for controlling the pH (e.g. ammonium hydroxide) and ammonia. Ammonium hydroxide when used, and indeed other additives, may provide the and/or an additional source of nitrogen.

Preferably, the total quantity of additives (excluding ammonia) is less than 5% by weight (excluding the weight of water present), more preferably less than 3% or less than 2% by weight.

It is preferred to include a silane as an additive. The binder and/or binder solution may comprise at least 0.1% and/or less than 1% of a silane by dry weight. The silane may be amino substituted; it may be a silyl ether and it is believed that its presence may significantly improve the long term strength of the binder, particularly after weathering.

Preferences for the pH of the binder are:

	Preferred	More preferred	Most preferred
pH of binder	≥ 7	≥ 8	≥ 9

at least in the state in which the binder is applied to a material to be bound and/or recovered in a waste water recuperation system. Such a neutral or alkaline pH of the binder may alleviate problems of corrosion of manufacturing equipment which have been encountered with some essentially acidic prior art binder systems. Such prior art binders include binders consisting essentially of polyacrylic acids or polymer polycarboxylic acids. One particular advantage of the present invention is thus the use of a binder system that can operate in such neutral or alkaline conditions. When cured, the binder may become acidic during the curing process. However, equipment corrosion considerations are less significant in this case due to the minimal contact between the manufacturing equipment and the binder when in this state. The pH of the binder may be less than or equal to 13, preferably less than or equal to 12, 11 or 10. A preferred pH may be in the range of 7.5 to 9.5, particularly 8 to 9.

It is preferred to arrange the pH of the binder solution at an appropriate level to prevent precipitation of its constituents and particularly to ensure that the acid precursor derivable from an inorganic salt remains in solution. This is particularly the case where ammonium phosphate provides the acid precursor. Better dry and/or weathered strengths and/or more homogeneous products may be achieved by using homogeneous binder solutions comprising ammonium salt acid precursors which are free from precipitates, particularly when ammonium phosphate is used and the binder solution is free from phosphate precipitates.

The binder composition may be provided in the form of an aqueous solution; it may contain free ammonia or excess ammonia in solution. A neutral or alkaline pH of the binder may be generated by an excess of alkaline groups compared with acid groups present in the binder solution, for example, due partially or substantially to the presence of ammonia in the solution. Additional ammonia may be added to the binder solution, for example 0.2%-1% by weight, or indeed more; this may help to keep a wash water system used in the manufacture of mineral wool insulation alkaline over the long term.

When binder solution is sprayed on to hot mineral wool fibres just after they have been formed, the residual heat of the mineral wool fibres may cause a significant portion of any water in the binder solution to evaporate. Consequently, the mineral wool fibres which are then collected to form a batt may have binder present on them in the form of a sticky, viscous or tacky liquid. This may facilitate bonding between individual fibres via the binder.

One of the many advantages of this binder system is that it is sprayed onto the mineral wool fibers in a substantially unreacted state. The ability to spray the binder solution onto the mineral wool fibers in a substantially unreacted state may alleviate problems associated with pre-reacting the binder components in solution which have been encountered with some prior art binder systems in which the components are pre-reacted. Such prior art binders include binders consisting essentially of pre-reacted polymers or resins which are applied to the materials to be bound. With substantially unreacted binder present on the mineral wool fibers in the form of a sticky, viscous or tacky liquid, the reaction between the binder components may occur in a substantially dry state. One may describe the reaction as a bulk polymerization because it is occurring without the benefit of a solvent. A particular advantage of the present invention is thus the use of a binder system that can polymerise in a substantially dry state or through a bulk polymerisation.

The mineral fibres may be formed by internal or external spinning. They may have a temperature in the range 20° C. to 200° C., generally 30° C. to 100° C. or 150° C., when sprayed with the binder solution. The quantity of binder solution sprayed may be used with or without additional water sprays to assist in cooling the mineral fibres to a desired temperature between their formation and their collection to form a bat.

A particular advantage of using ammonia in solution to control the pH of the binder solution applied to the mineral fibres is that at least part of the ammonia of binder solution that sticks to the fibres may flash off due to the residual heat of the mineral wool fibres. Consequently, the binder solution that coats the fibres may have a lower pH than the binder solution sprayed.

The binder may be curable; it may be cured, for example in a curing oven; it may form a thermoset binder. In its cured form, the binder may: comprise melanoidins; and/or be thermoset; and/or be water insoluble or substantially water

insoluble. The binder solution may be substantially colourless or white to off-white; upon curing, the binder may take on a dark colour, particularly a dark brown colour. The cured product may be dark in colour, particularly dark brown in colour. The binder may be free of proteins; it may be free of cellulosic feedstock. One of the many advantages of this binder system is that the extent of curing can be determined by the colour. Substantially dehydrated binder appears white or off-white. Progressively cured to a greater extent, the binder appears progressively darker in colour (a darker shade of brown). When applied to mineral fibers, the extent to which the mineral wool insulation has cured can be determined by its colour.

When applied to the mineral fibres and/or prior to passing through the curing oven, the binder may be free or substantially free of melanoidins and/or other reaction products derived from curing. Curing of the binder may produce glucosylamine, particularly as an intermediate product. Consequently, a cured or particularly a partially cured product may comprise glucosylamine.

The reaction of the binder upon curing may be essentially a Maillard type reaction as described for example in US Patent Application 20070027283 or WO2007/14236. The binder may comprise polymerisation products of a mixture that comprises a reducing sugar and a material selected from the group consisting of ammonium sulphate, ammonium phosphate, ammonium nitrate and ammonium carbonate.

The binder solution may be formulated by combining:

A carbohydrate, preferably a reducing sugar;

An acid precursor derivable from an inorganic salt, preferably an ammonium sulphate or ammonium phosphate;

A source of nitrogen; and
water.

The formulation may comprise optional or additional ammonia provided in the form of an aqueous ammonia solution. The water may comprise wash water.

Forming the binder solution from a carbohydrate and an acid precursor comprising an inorganic ammonium salt provides one particular advantageous preparation method. This may be achieved in a simple mixing chamber which may be open and/or at atmospheric pressure. The carbohydrate and/or the acid precursor may be added in powder or liquid form. The preparation is preferably carried out at room temperature. Preferably it is not necessary to supply heat to prepare the binder solution; nevertheless, the binder solution may be heated during its preparation, for example to a temperature with the range 20° C. to 80° C., particularly where this facilitates dissolving and/or mixing of its ingredients.

The binder solution may comprise:

at least 5% 10%, 15% or 18% solids and/or

less than 50%, 40% or 20% solids particularly determined as bake out solids by weight after drying at 140° C. for 2 hours.

The binder solution and/or the binder are preferably organic.

The mineral fibre insulation may be shaped and/or dimensioned and/or moulded with the aid of the binder.

The binder solution, particularly when applied to the mineral fibres, may have a viscosity appropriate for application by spraying or pouring. Its viscosity at 20° C. may be:

Less than about 1.5 Pa·s, preferably less than about 1×10^{-2} Pa·s; and/or

Greater than about 2×10^{-4} Pa·s, preferably greater than about 5×10^{-4} Pa·s

Curing of the binder may occur in a curing oven, for example using forced hot air circulation; it may occur in a press. Curing may comprise a dehydration of the binder; it may comprise a polymerisation. Curing may comprise a bulk polymerisation reaction. Curing may be carried out for duration of 20 minutes or less, preferably 10 minutes or less. Curing of the binder preferably occurs when the binder solution (from which water may have been evaporated) is in contact with the mineral fibres; it may occur at substantially atmospheric pressure. The curing may be a substantially dry curing, that is to say by application of dry heat and/or substantially dry or heated atmospheric air rather than using steam or heated water vapour.

The curing temperature and time may be selected as a function of the product density and/or thickness. The curing oven in such cases may have a plurality of heating zones having temperatures within the range 200° C. to 350° C. (typically 230° C. to 300° C.). A thin, low density product (12 kg/m³ or less) may be cured by passing through the curing oven in as little as 20 seconds; a thick, high density product (80 kg/m³ or more) may require a passage of 15 minutes or more in the curing oven. The product may reach a temperature in the range 180° C.-220° C. during the curing process.

The cured binder may comprise greater than 2% and/or less than 8% nitrogen by mass as determined by elemental analysis.

The binder in its uncured state may comprise the following levels of sulphates, phosphates carbonates and/or nitrates by dry weight:

Greater than 2.5%, 3% or 5%; and/or

Less than 25%, 22%, or 20%

Finished materials manufactured using binder systems according to the present invention may have residual levels of sulphates, phosphates, carbonates and/or nitrates derived notably from the inorganic salt serving as the acid precursor. Such species may be present in the following quantities:

Greater than 500, 750, 1000 or 1500 mg/kg; and/or

Less than 5000, 4000 or 3000 mg/kg.

The presence of such species may be assessed in a leach test and provide an indication in the final product of the binder system used.

The quantity of binder in the finished product may be:

Greater than: 1%, 2%, 2.5%, 3%, 3.5% or 4%; and/or

Less than: 20%, 15%, 10% or 8%

measured by dry weight of the finished product.

The mineral wool insulation may have one or more of the following parting strengths:

Ordinary Parting Strength of

At least 120 g/g, preferably at least 150 g/g; and/or

Less than 400 g/g

Weathered Parting Strength of

At least 120 g/g, preferably at least 150 g/g; and/or

Less than 400 g/g

% loss between Ordinary and Weathered Parting Strength of

Less than 10%, preferably less than 5%

The mineral wool insulation may have one or more of the following characteristics:

A density greater than 5, 8 or 10 kg/m³;

A density less than 200, 180 or 150 kg/m³

Comprise glass wool fibres and have a density greater than 5, 8 or 10 kg/m³ and/or less than 80, 60 or 50 kg/m³;

Comprise stone wool fibres and have a density greater than 15, 20 or 25 kg/m³ and/or less than 220, 200 or 180 kg/m³;

A thermal conductivity A of less than 0.05 W/mK and/or greater than 0.02 W/mK

Comprise less than 99% by weight and/or more than 80% by weight mineral fibres.

A thickness of greater than 10 mm, 15 mm or 20 mm and/or less than 400 mm, 350 mm or 300 mm.

Embodiments of the invention will now be described by way of example with reference to FIG. 1 which is a plan view of a test sample.

Shell Bone Testing:

Binders were prepared as aqueous solutions by combining the ingredients of a desired binder formulation in an open, unheated reaction vessel

adding distilled water

subsequently adding a silane solution

agitating during addition of liquids and afterwards for several minutes to achieve complete dissolution of solids

such that the binder solution contained approximately 45% dissolved solids as a percentage of total weight of solution. A 2-g sample of this solution, upon thermal curing at about 200° C. to 210° C. for 8 minutes, would yield 30% solids (the weight loss being attributed to dehydration during thermoset binder formation).

An evaluation of dry and "weathered" tensile strength of glass bead-containing shell bones provided an indication of the likely tensile strength and the likely durability of fibre-glass insulation or other materials prepared with that particular binder. Predicted durability is based on the ratio of a shell bone's weathered tensile strength to its dry tensile strength.

To prepare the shell bones, an electric mixer was used for about two minutes to mix approximately 75 g of binder with 727.5 g of glass beads (equivalent to Quality Ballotini Impact Beads, Spec. AD, US Sieve 70-140, 106-212 micron-#7, from Potters Industries, Inc.). Any clumps from the sides of the mixer whisk and from the sides and bottom of the mixing bowl were mixed in manually using a spatula about half way through the mixing and also at the end of the mixing.

The prepared glass beads/binder mixture was added to the mould cavities of a shell bone mould (Dietert Foundry Testing Equipment; Heated Shell Curing Accessory, Model 366) which had been pre-heated to about 218° C. (425° F.). The surface of the mixture in each cavity was flattened out, while scraping off the excess mixture to give a uniform surface area to the shell bone. Any inconsistencies or gaps that existed in any of the cavities were filled in with additional glass beads/binder mixture and then flattened out. The top platen was quickly placed onto the bottom platen (to avoid producing shell bones with two differentially cured layers). The cured shell bones were removed after seven minutes, cooled to room temperature on a wire rack, labelled and placed individually in plastic storage bags. If shell bones could not be tested on the day they were prepared, the shell bone-containing plastic bags were placed in a desiccator unit. During curing the temperature of the bottom platen ranged from about 204° C. to about 221° C. (about 400° F. to about 430° F.), while the temperature of the top platen ranged from about 227° C. to about 243° C. (about 440° F. to about 470° F.).

Procedure for Testing Breaking Strength:

Equipment: 5500 R Instron machine

Immediately prior to testing, each shell bone was removed from its plastic bag and its weight and thickness recorded.

Weathering Procedure for Shell Bones:

16 hours weathering in a pre-heated humidity chamber (65° C., 95% relative humidity)

upon removal shell bones were sealed in individual plastic storage bags and taken immediately for testing.

Procedure for Measuring Gel Time:

A small amount of binder (2.0 ml) is added to the centre of a hot plate set to 150° C. and a stop watch is started. The binder is worked with a spatula until it is possible to draw the sample into a long string. The time taken from the addition of the binder to the string formation is the gel time.

Binder Formulations Tested—Inorganic Acid Precursors Compared with Citric Acid:

Test ref:	Binder formulation (by dry weight)
A	85% DMH + 15% CA + 4.8% NH4OH + 0.3% ISIO200
B	90% DMH + 10% AmSO4 + 4.8% NH4OH + 0.3% ISIO200
C	85% DMH + 15% AmSO4 + 4.8% NH4OH + 0.3% ISIO200
D	80% DMH + 20% AmSO4 + 4.8% NH4OH + 0.3% ISIO200
E	90% DMH + 10% AmPO4 + 4.8% NH4OH + 0.3% ISIO200
F	85% DMH + 15% AmPO4 + 4.8% NH4OH + 0.3% ISIO200
G	80% DMH + 20% AmPO4 + 4.8% NH4OH + 0.3% ISIO200

Binder Formulations Tested—Combined Inorganic Acid Precursor and Citric Acid Compared with Citric Acid Alone and Inorganic Acid Precursor Alone:

Test ref:	Binder formulation (by dry weight)
H	85% DMH + 15% CA + 4.8% NH4OH + 0.3% ISIO200
I	85% DMH + 10% CA + 5% AmSO4 + 4.8% NH4OH + 0.3% ISIO200
J	85% DMH + 5% CA + 10% AmSO4 + 4.8% NH4OH + 0.3% ISIO200
K	85% DMH + 15% AmSO4 + 4.8% NH4OH + 0.3% ISIO200

Key:
 DMH = Dextrose monohydrate
 CA = citric acid
 NH4OH = ammonium hydroxide
 ISIO200 = silane
 AmSO4 = ammonium sulphate
 AmPO4 = ammonium phosphate

Test Results—Inorganic Acid Precursors Compared with Citric Acid:

Test ref	Dry breaking strength (MN/m ²)	Weathered breaking strength (MN/m ²)	Loss in breaking strength from weathering/ %	Gel time of binder solution (s)	pH of binder solution just before mixing with beads
A	1.455	1.567	-7.70	343	9.54
B	1.271	0.895	29.57	280	10.28
C	1.550	0.856	44.79	362	10.24
D	1.877	1.156	38.39	327	10.13
E	1.499	1.069	28.68	356	10.18
F	1.281	0.848	33.82	334	9.99
G	1.123	0.801	28.74	287	9.73

Test Results—Combined Inorganic Acid Precursor and Citric Acid Compared with Citric Acid Alone and Inorganic Acid Precursor Alone:

Test ref	Dry breaking strength (MN/m ²)	Weathered breaking strength (MN/m ²)	Loss in breaking strength from weathering/ %	Gel time of binder solution (s)	pH of binder solution just before mixing with beads
H	1.69	1.50	11.32	363	9.39
I	1.50	1.18	21.37	341	9.71
J	1.21	1.05	13.19	375	9.99
K	1.47	1.02	30.33	376	9.97

Results from tests carried out together (test A to G were carried out in one session and tests H to K carried out during another session) provide a useful indication of results relative to other results obtained during the same test session. It may not be reliable to compare tests results from different test sessions.

First Comparative Testing on Insulation Product:

Comparative testing of binder systems on a mineral fibre insulation product gave the following results:

Binder tested	Description	Formulation
PF1	Comparative example - standard phenol formaldehyde binder	Resin, Urea, Lignin, Ammonia, Silane
AC1	Comparative example - ammonium citrate based binder	Dextrose 85% Citric Acid 15% Ammonia 4.8% Silane 0.3%
Ex1	Example 1 of the present invention	Dextrose 85% Ammonium Sulphate 15% Ammonia 4.8% Silane 0.3%
Product used for test:	glass wool fibre insulation product, nominal density 16 kg/m ³ , nominal thickness 75 mm, nominal width 455 mm	

Binder Content of Test Product LOI (Loss on Ignition) % Weight:

Binder	Mean LOI
PF1	6.22%
AC1	6.91%
Ex1	6.78%

Drape Test (Mean Average in mm Measured after the Periods Specified):

Binder	Day 1	Week 1	Week 3	Week 6
PF1	55	68	60	71
AC1	83	99	80	72
Ex1	66	76	66	75

Thickness (Mean Average in mm Measured after the Periods Specified in accordance with British Standard BS EN 823: 1995)

Binder	Day 1	Week 1	Week 3	Week 6
PF1	76.4	75.1	75.1	75.2
AC1	75.3	73.6	72.5	74
Ex1	76	76.7	74.9	74.3

Density (Mean Average in kg/m³ Measured After the Periods Specified)

Binder	Day 1	Week 1	Week 3	Week 6
PF1	16.44	16.7	16.35	16.44
AC1	16.68	16.41	16.33	16.48
Ex1	16.5	16.9	16.5	16.5

Quantity of Sulphates Present mg/kg

Binder	Sample 1	Sample 2
AC1	240	240
Ex1	2000	2200

Parting Strength (g/g)

Binder	Ordinary	Weathered	% loss
PF1	248	107	56.85
AC1	230	199	13.47
Ex1	196	189	3.57

Test Procedures:

Binder Content LOI (Loss on Ignition)

A weighed sample of wool plus binder is placed in a muffle furnace set to 550° C. After a set time the wool is removed from the furnace, placed in a desiccator to cool and re-weighed. The weight loss is expressed as a percentage of the original sample weight and is known as the binder content or Loss On Ignition (LOI).

Drape Test

A single batt (or slab) is placed across two poles (each 500 mm long, 20 mm diameter) set into a wall 1 meter apart. The degree of sag in the centre of the batt is recorded. This is repeated for all of the batts in a pack and for several packs. Packs are measured at set points over a period of time to determine the long term effects of compression on the batts.

Density: Measured for the Samples Subjected to the Drape Test

Quantity of sulphates present: leaching test for granular wastes in water with eluate analysis according to British standard BS EN 12457-2 at L/S10

Parting Strength

The parting strength is expressed in grams/gram being the total breaking load of six test specimens divided by their total weight.

The test is carried out on mineral fibre mats as received for testing (Ordinary Parting Strength) and after an accelerated weathering test as explained below (Weathered Parting Strength).

A first set of six samples of the form and dimensions shown in FIG. 1 are cut from the mineral fibre mat to be tested. The dimensions are:

r: radius 12.7 mm;
DC: distance between centres 44.5 mm;
a: 25.4 mm;
b: 121 mm.

The long axis of the samples should be parallel to the conveyor direction and the samples should be taken across the full width of the mineral mat. A second set of six samples is then taken in the same way.

The total weight of the first group of six samples W1 in grams is recorded. The total weight of the second group of six samples W2 in grams is recorded; these samples are then placed in a preheated autoclave and conditioned on a wire mesh shelf away from the bottom of the chamber under wet steam at 35 kN/m² for one hour. They are then removed, dried in an oven at 100° C. for five minutes and tested immediately for parting strength.

To test the parting strength, each sample is mounted in turn on the jaws of a 5500 Instron tensile strength machine and the maximum breaking load in grams or Newtons is recorded. If the breaking load is measured in Newtons it is converted to grams by multiplying it by 101.9. Six results in grams are obtained for each set of samples: G1 G2 G3 G4 G5 and G6 for the first set of samples and G7 G8 G9 G10 G11 and G12 for the second set of samples. The Ordinary Parting Strength is calculated from the first set of samples using the formula Ordinary Parting Strength=(G1+G2+G3+G4+G5+G6)/W1.

The Weathered Parting Strength is calculated from the second set of samples using the formula Weathered Parting Strength=(G7+G8+G9+G10+G11+G12)/W2.

Second Comparative Testing on Insulation Product:

Product used for test:	glass wool fibre insulation product, nominal density 7.2 kg/m ³ , nominal thickness 159 mm
------------------------	---

Samples: The Following Samples of Fibreglass Batts were Tested:

Example	Binder Description	Target binder content (LOI) for product
PF2	standard phenol formaldehyde binder of Resin, Urea, Ammonia, Silane	4.5%
2.1	Dextrose 85% Ammonium Sulphate 15% Silane 0.3% (10.6% solids in binder solution)	4.5%
2.2	Dextrose 85% Ammonium Sulphate 15% Silane 0.3% Norjoh oil (11.4% solids in binder solution)	4.5%
2.3	Dextrose 85% Ammonium Sulphate 15% Silane 0.3%, 2.4% NH3 (10.6% solids in binder solution)	4.5%
2.4	Dextrose 85% Ammonium Sulphate 15% Silane 0.3%, 2.4% NH3 (10.6% solids in binder solution)	6.0%

Results

	PF2	2.1	2.2	2.3	2.4
Recovery	158 mm	157 mm	163 mm	160 mm	166 mm
Recovery, % nominal	99.4%	99.0%	102.8%	100.6%	104.8%
Parting Strength (ASTM C-686)	190.8 g/g	131.7 g/g	146.7 g/g	159.9 g/g	143.9 g/g
Parting strength after	145.9 g/g	100.0 g/g	110.3 g/g	124.9 g/g	114.3 g/g

-continued

	PF2	2.1	2.2	2.3	2.4
weathering (ASTM C-686 following conditioning for 7 days at 90° F., 90% relative humidity)					

What is claimed is:

1. A method of manufacturing a glass fibre thermal insulation product which comprises less than 99% by weight and more than 80% by weight glass fibres and has a density greater than 5 kg/m³ and less than 80 kg/m³, the method comprising sequentially:

forming glass fibres from a molten mineral mixture; spraying a substantially formaldehyde-free binder solution onto the glass fibres;

collecting the glass fibres to which the binder solution has been applied to form a batt of glass fibres; and curing the batt comprising the glass fibres and the binder by passing the batt through a curing oven so as to provide a batt of glass fibres held together by a cured, thermoset, substantially formaldehyde-free, nitrogenous polymer-containing binder,

wherein the binder solution consists essentially of (i) a carbohydrate reactant comprising a reducing sugar or a carbohydrate reactant that yields a reducing sugar in situ under thermal curing conditions and (ii) an acid precursor, in aqueous solution,

wherein the acid precursor provides (i) ionic species selected from the group consisting of sulphates, phosphates, nitrates and combinations thereof and ii) an amine or amine reactant.

2. The method of claim 1, in which wash water is sprayed onto the glass fibres between their formation and their collection to form a batt, at least a part of the wash water having been sprayed onto glass fibres and subsequently returned to a wash water system to be reused as wash water.

3. The method of claim 1, in which the binder solution is sprayed onto the glass fibres when the glass fibres are at a temperature of between 30° C. and 150° C.

4. The method of claim 1, in which curing of the binder is carried out by passing the batt through at least one zone of a curing oven at a temperature within the range 230° C.—300° C. with an oven residence time in the range 30 seconds to 20 minutes.

5. The method of claim 1, in which the binder solution has a pH of greater than 7 when sprayed onto the glass fibres.

6. The method of claim 1, in which the acid precursor makes up between 5% and 25% by dry weight of the binder solution.

7. The method of claim 1, in which the acid precursor comprises an inorganic salt.

8. The method of claim 1, in which the carbohydrate reactant of the binder solution comprises a reducing sugar which has a dextrose equivalent value of at least 0.85.

9. The method of claim 1, in which the carbohydrate reactant of the binder solution consists essentially of dextrose.

10. The method of claim 1, in which the binder solution comprises a silicon containing compound.

11. The method of claim 1, in which the binder solution comprises a material selected from the group consisting of a polycarboxylic acid, a salt of a polycarboxylic acid, and an anhydride of a polycarboxylic acid.

12. The method of claim 1, in which the binder solution comprises excess ammonia.

13. The method of claim 12, in which the binder solution has a pH which, in its conditions of use, prevents precipitation of sulphates or phosphates.

14. The method of claim 1, in which there is at least 7% by dry weight of the acid precursor with respect to reducing sugar.

15. The method of claim 1, in which the ratio by dry weight of reducing sugar to acid precursor (expressed as dry weight of reducing sugar/dry weight of acid precursor) is in the range 2.5 to 13.

16. The method of claim 1, in which the cured binder comprises melanoidins.

17. The method of claim 1, in which the quantity of binder in the glass fibre thermal insulation product is greater than 1% and less than 15% measured by dry weight of the glass fibre thermal insulation product.

18. The method of claim 1, wherein the glass fibre thermal insulation product comprises residual levels of more than 500 mg of ionic species per kg of product, said species selected from the group consisting of sulphates, phosphates, nitrates and combinations thereof, in which the residual levels are assessed in a leach test.

19. The method of claim 1, wherein the glass fibre thermal insulation product comprises residual levels of more than 750 mg of ionic species per kg of product, said species selected from the group consisting of sulphates, phosphates, nitrates and combinations thereof, in which the residual levels are assessed in a leach test.

20. The method of claim 1, wherein the glass fibre thermal insulation product comprises residual levels of less than 5000 mg of ionic species per kg of product, said species selected from the group consisting of sulphates, phosphates, nitrates and combinations thereof, in which the residual levels are assessed in a leach test.

21. The method of claim 1, in which the cured binder is substantially water insoluble.

22. The method of claim 1, in which the cured binder has a dark brown color.

23. The method of claim 1, in which the cured binder comprises greater than 2% nitrogen by mass.

24. The method of claim 1, in which the cured binder comprises less than 8% nitrogen by mass.

25. The method of claim 1, in which the reaction of the binder upon curing is essentially a Maillard type reaction.

26. The method of claim 1, in which the binder solution as sprayed onto the glass fibres comprises at least 5% solids.

27. The method of claim 1, in which the binder solution as sprayed onto the glass fibres comprises at least 10% solids.

28. The method of claim 1, in which the binder solution as sprayed onto the glass fibres comprises levels of sulphates, phosphates, nitrates, or combinations thereof by dry weight that are greater than 2.5%.

29. The method of claim 1, in which the binder solution as sprayed onto the glass fibres comprises levels of sul-

15

phates, phosphates, nitrates, or combinations thereof by dry weight that are greater than 3%.

30. The method of claim 1, in which the binder solution as sprayed onto the glass fibres comprises levels of sulphates, phosphates, nitrates, or combinations thereof by dry weight that are greater than 5%.

31. The method of claim 1, in which the binder solution as sprayed onto the glass fibres comprises less than 40% solids.

32. The method of claim 1, in which the binder solution as sprayed onto the glass fibres comprises levels of sulphates, phosphates, nitrates, or combinations thereof by dry weight that are less than 25%.

33. The method of claim 1, in which the acid precursor comprises an ammonium salt.

34. The method of claim 1, in which the glass fibre thermal insulation product has an Ordinary Parting Strength of at least 120 g/g and less than 400 g/g.

35. The method of claim 1, in which the spraying of substantially formaldehyde-free aqueous binder solution onto the glass fibres comprises spraying the substantially formaldehyde-free aqueous binder solution onto the glass fibres just after the glass fibres have been formed so that the residual heat from the glass fibres causes a significant portion of the water in the aqueous binder solution to evaporate.

36. The method of claim 1, in which glass fibres are formed by internal spinning.

37. The method of claim 1, in which the glass fibre thermal insulation product has i) an ordinary parting strength which is at least 120 g/g and less than 400 g/g and ii) a weathered parting strength which is at least 120 g/g and less than 400 g/g.

38. The method of claim 1, in which the glass fibre thermal insulation product has a thickness of greater than 15 mm and less than 350 mm.

39. The method of claim 1, in which the glass fibre thermal insulation product has a thermal conductivity λ of less than 0.05 W/mK and greater than 0.02 W/mK.

40. The method of claim 1, further comprising compressing the cured bans in a pack.

41. The method of claim 1, wherein the binder solution includes at least one additive selected from: silanes, mineral oils, coupling agents, silicones, siloxanes, surfactants, hydrophilic additives, hydrophobic additives and waxes.

42. The method of claim 1, wherein the total quantity of the additives is less than 5% by weight excluding the weight of water present.

16

43. The method of claim 1, wherein the binder solution comprises between 0.1% and 1% of a silane or silicon-containing coupling agent calculated as dissolved binder solids.

44. A method of manufacturing a glass fibre thermal insulation product which comprises less than 99% by weight and more than 80% by weight glass fibres and has a density greater than 5 kg/m³ and less than 80 kg/m³, the method comprising sequentially:

- forming glass fibres from a molten mineral mixture;
- spraying a substantially formaldehyde-free aqueous binder solution onto the glass fibres just after they have been formed so that the residual heat from the glass fibres causes a significant portion of the water in the aqueous binder solution to evaporate;
- collecting the glass fibres to which the binder solution has been applied to form a batt of glass fibres; and
- curing the batt comprising the glass fibres and the binder by passing the batt through a curing oven for a duration of 20 minutes or less using forced hot air convection so as to provide a batt of glass fibres held together by a cured, thermoset, substantially formaldehyde-free, nitrogenous polymer-containing binder,

wherein the binder solution consists essentially of (i) a carbohydrate reactant comprising a reducing sugar or a carbohydrate reactant that yields a reducing sugar in situ under thermal curing conditions and (ii) an acid precursor, in aqueous solution;

wherein the acid precursor makes up at least 7% by dry weight of the uncured binder solution,

and wherein the acid precursor provides (i) ionic species comprising sulphates and/or phosphates and ii) an amine or amine reactant.

45. The method of claim 44, in which the ratio by dry weight of the reducing sugar to the acid precursor (expressed as dry weight of reducing sugar/ dry weight of acid precursor) is in the range 2.5 to 13.

46. The method of claim 44, further comprising compressing the cured bans in a pack.

47. The method of claim 44, in which the acid precursor comprises an ammonium salt.

48. The method of claim 47, wherein the ammonium salt comprises an ammonium sulphate salt.

49. The method of claim 47, wherein the ammonium salt comprises an ammonium phosphate salt.

50. The method of claim 33, wherein the ammonium salt comprises an ammonium sulphate salt.

51. The method of claim 33, wherein the ammonium salt comprises an ammonium phosphate salt.

* * * * *